

MECHANISMS INVOLVED IN THE POLYMERIZATION OF
CONJUGATED AND NONCONJUGATED
LINOLEIC ACID

by

CHANG SZU SHIANG

B. S., National Chi-nan University
Shanghai, China, 1941

A THESIS

submitted in partial fulfillment of the
requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

1949

Docu-
ment
LD
2668
T4
1949
S51
C.2

TABLE OF CONTENTS

INTRODUCTIONS	1
EXPERIMENTAL	11
Preparation of Materials	11
Polymerization Process	15
Depolymerization Processes	16
Determination of Constants	18
RESULTS	25
Change in Molecular Weight and Neutral Equivalent	
During Autoxidation	25
Effectiveness of the Depolymerization Processes	25
Products of Molecular Distillation	28
DISCUSSION	30
The Formation of Trimers by Linoleic acid	30
The Role of Carboxyl Group in the Polymerization	
of Linoleic acid	30
The Differences in the Mechanisms Involved in the	
Polymerization of Conjugated and Nonconju-	
gated Linoleic acid	32
SUMMARY	34
ACKNOWLEDGMENT	35
LITERATURE CITED	36

INTRODUCTION

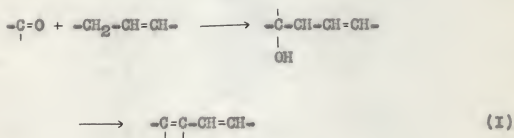
The reaction of unsaturated fatty materials with oxygen involves oxidation as well as polymerization. Many studies have been made on the mechanisms involved in the autoxidation of drying oils during recent years (1, 12, 13, 21, 22). The explanation of the initial steps has been well established. The polymerization of oils induced by oxidation is now recognized as the process responsible for the drying of oil films. However, the polymers formed still remain uncharacterized and their mechanism of formation uncertain.

Bradley (4, 5), developed the theory of functionality as applied to film formation, oil bodying and related phenomena. This theory is now generally accepted. According to this theory, a minimum number of functional groups are required to be present in the reacting substance in order that polymer formation may occur. In the case of the fatty acids, the functional groups may be unsaturated linkages, hydroxyl groups and carboxyl groups. Thus, if double bonds only are present then only additional polymerization is possible, and if only hydroxyl and carboxyl groups are present, only condensation reactions are possible. When both types of functional groups are present, both types of polymerization can occur. However, the formation of a solid film by three dimensional polymerization required at least three functional groups. This explains why linoleic acid and its methyl esters could form viscous polymers

only, while its glycol and glycerol esters could form solid film.

In the case of linoleic acid, there are two functional groups present, the double bond and the carboxyl group. Its polymerization may therefore result from either one of the two functional groups or from both of them. Various mechanisms have been suggested to explain the drying property of linoleic acid, all of them have certain background and proof. However, none of them is quite satisfactory, and none could be supported with enough experimental evidence to make it generally accepted.

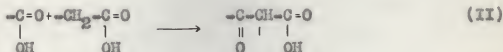
The polymerization of linoleic acid due to the carboxyl group may be accomplished by aldol condensation as well as by direct dehydration. Holman, Lundburg and Burr (12) suggested the aldol condensation between a carboxyl group in one chain and a methylene group in a second.



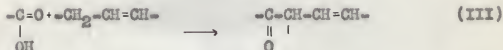
They believed that this type of bond is the cause of chromophore development in oxidized oil. However, changes in physical and chemical properties accompanying the polymerization step indicate that aldol formation is not the principal step responsible for the polymerization of drying oils. The negligible tendency for oleic acid to polymerize is difficult to explain with this

mechanism.

The other type of condensation may be accomplished by the condensation of the carboxyl group in one segment and the activated methylene group of another segment. The methylene group may be activated by the double bond or by the carboxyl group (9, p. 44).



or



However, neither this type of polymerization nor an aldol condensation seemed to be the principal reaction involved in the drying of unsaturated oils. Burk et al. (9, p. 44) pointed out that when the carbonyl group occurs in a carboxyl or ester group, its polymerizing powers are substantially suppressed. Thus, the polymerizing power of the fatty acids is confined to the loose association type of binding and even this power is lost largely in the case of fatty esters.

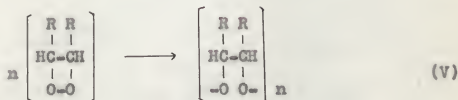
There are two possible routes of polymerization which involve the double bond; one, a carbon to carbon, and two, a carbon to oxygen bond. The carbon to carbon linkage may possibly be produced by three different ways. First, open chain polymers resulting from the vinyl bonding of two of the un-

saturated groups in adjacent fatty acid segments; second, cyclic chain polymers through bridges involving the Diels-Alder type addition of two of the unsaturated groups in adjacent fatty acid segments; and third, open chain polymers formed by the adol condensation between an activated methylene group and a carbonyl group which may result from the decomposition of a peroxide. The carbon to oxygen linkage may possibly be produced either by a dioxane ring resulting from the joining of one double bond to a peroxide group of an adjacent oxidized fatty acid segment; or by a peridioxane ring resulting from the bonding of a peroxide group in one oxidized fatty acid molecule with another peroxide group in an adjacent segment. A brief survey of the above mentioned types of polymerization is given below.

The peroxide groups of two oxidized acid molecules may be hooked together according to the following scheme (21).



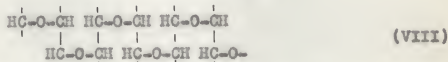
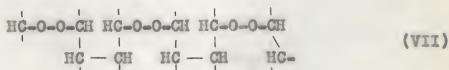
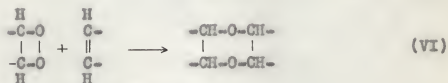
and



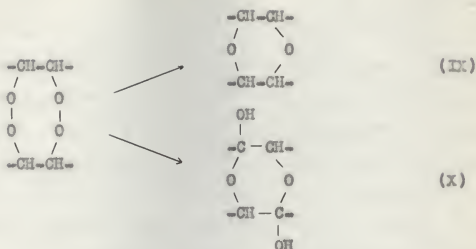
Reaction IV, proposed by Goldschmidt and Freund, according to Dean, (10, p. 218), does not account for the rapid decrease in iodine value and specific refraction during the polymerization stage. Further oxidation of unsaturated compounds can not

account for the drop in iodine value and specific refraction. There is no reason why the rate of oxygen absorption during this stage should be greater than during the first stage, and furthermore, ultimate analyses and gain in weight measurements do not indicate an abnormally rapid oxygen absorption. The same arguments seem to rule out the possibility of the peroxide polymers as represented by formula V, which is suggested by Staudinger et al., (24).

When peroxide groups combine with unoxidized double linkages, two mechanisms are possible. One would be a dioxane derivative, formula VI, while the other would be a chain polymer containing alternate C-O-O-C and new C-C linkages, formula VII, or alternate C-O-C and C-C linkages, formula VIII.



The structure VI could also be formed by the rearrangement or decomposition of a peroxane ring (22, 27, 28).

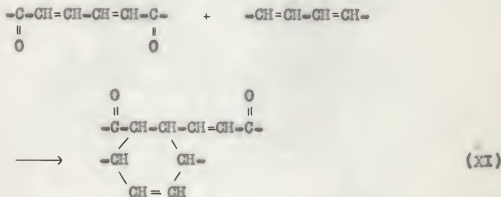


There are several serious objections to this mechanism (22). There has never been any explanation offered of why it does not operate in the case of oleic esters, which show a negligible tendency to polymerize under usual conditions. The mechanism of such a reaction should be exceedingly complex to the point of being improbable. A peroxide formed at the double bond would have to combine with an unsaturated group on another fatty acid segment, the second mole of oxygen would then add and complete the ring. The probability of two molecules of oxygen and two unsaturated groups arriving at the required arrangement in space at the same time is too remote for serious consideration. Other objections to this theory include the fact that the presence of the dioxane ring has never been established in oxidized oils (11), also the only evidence for the presence of the necessary amount of ether oxygen is indirect and inconclusive.

The probable formation of carbon to carbon linked polymers receives considerable support from the observation that there

are only insignificant differences between the amount of oxygen found in the oxidized drying oil esters by ultimate analyses and the sum of oxygen present in ether, peroxide, aldehyde and hydroxyl groups (6, 19, 20). Overholt and Elm (18) studied the autoxidation of conjugated compounds, while Bolland and Koch (2) studied the autoxidation of nonconjugated compounds. Independently these authors concluded that the role of oxygen is only a peroxidic catalyst for the carbon to carbon linked polymerization.

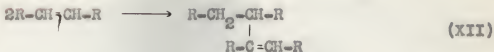
Kappelmeier (14) suggested that the polymerization took place by a diene or 1,4 addition reaction of a conjugated segment of fatty acid with double bond of another molecule to form a substituted cyclo-hexene derivatives. This theory is strongly supported by Bradley and co-workers (7). They investigated the constituents of drying oil gels and isolated and characterized a fraction of polybasic acid which they termed dimeric acid. According to the postulated mechanism, the structural formula for this dimerized conjugated diene acid should be:



For nonconjugated diene acids, one segment is isomerized first to conjugated double bond, and it will then undergo a diene reaction with a nonconjugated double bond of another unisomerized molecule.

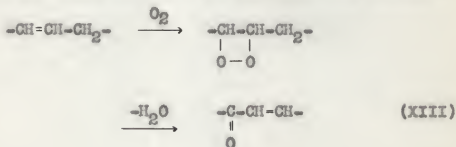
The weight of evidence accumulated on the behavior of oxidized oils now seems to favor this view above all the others. It has been shown that the loss of unsaturation, increase in density, and drop in molecular refractivity accompanying the drying of unsaturated esters might well be interpreted as reflecting bonding of this type. Spectroscopic evidence points to the presence of carbonyl groups adjacent to carbon to carbon double bonds, of carbon to carbon double bonds with carbonyl groups alpha to both carbon atoms, and of a considerable content of conjugated dienes. Such systems might readily be expected to enter into a Diels Alder reaction. The change in density and specific refraction with little change in oxygen content are in agreement with this type of reaction than is vinyl polymerization.

Another possible type of carbon to carbon linked polymerization might result from a combination of two of the unsaturated groups in adjacent fatty acid segments by vinyl polymerization (21). The oxygen serves only to activate neighbouring double linkages. The latter may then enter into the vinyl polymerization according to the following scheme:



The pronounced change in density, decrease in iodine value, and decrease in refractivity accompanying the drying of films with little change in oxygen content are indicative of such a mechanism. It was shown that linoleic acid shows these changes to a more pronounced degree than do linolenic esters. This might be expected since two double bonds are sufficient to give air drying properties, with linolenic acid the third double bond affords a site for further oxidation which partially masks the effect of the polymerization reaction. Powers (22), in a recent article, further proved this mechanism by determining the density and refractivity changes, also the carbon and hydrogen content of linseed oil blown at 80°C.

The third possible mechanisms by which carbon to carbon polymers are formed involves an aldol condensation between a carbonyl group in one chain and an activated methylene group in a second chain. The carbonyl group is formed from the decomposition of a peroxide group according to the following scheme:



The scheme for the aldol condensation is the same as reaction I. The objections to the first mechanism could also be applied to this mechanism.

Very recently, Swern, Scanlan, and Knight (26), in reviewing the mechanisms of the reactions of oxygen with fatty materials, suggested that the polymers obtained in the air oxidation of linoleates probably consist of a mixture of carbon to carbon and oxygen linked compounds. However, they failed to give any experimental evidence to support their suggestion.

The purpose of the present investigation is an attempt to add to the understanding of the mechanisms of polymerization reaction involved in the drying and aging of unsaturated fatty acids through a new technique by trying to depolymerize the oxidized polymers and characterize the products.

EXPERIMENTAL

Preparation of Materials

The 9, 12 linoleic acid used in this investigation was obtained from the ethyl ester which was prepared by the debromination of tetrabromostearic acid by the Rollett method (23) as modified in this laboratory. The crystalline 10, 12 linoleic acid was prepared by the modified method of Van Mikusch (29) from dehydrated castor oil.

Preparation of the Fatty Acids. Three hundred g of potassium hydroxide were placed in a five liter round bottom flask, 1200 ml of ethyl alcohol and 100 ml of water were added, and the mixture was heated to near boiling on a steam bath. One hundred g of cottonseed oil were added to the hot solution, condenser attached, and refluxing allowed to proceed for 30 minutes. The hydrolysate was cooled to about 40° in a stream of tap water and 1300 ml of cold distilled water added. With continued cooling and agitation, 550 ml of cold concentrated hydrochloric acid were added in small portions. The cold mixture was then transferred to a large separatory funnel and shaken vigorously to insure complete decomposition of the soaps. The fatty acids were washed twice with about one liter of distilled water, care being taken to avoid emulsification. One liter of redistilled petroleum ether was added and the fatty acids were washed again. After the water had been drawn off the fatty acids were placed in a five liter round bottom flask

to which about 50 g of anhydrous sodium sulfate were added. One liter of redistilled petroleum ether was then added and the solution allowed to stand overnight at -5°C . The saturated acids and the sodium sulfate were filtered off and one liter of redistilled petroleum ether was added to the filtrate, which was then ready for bromination.

Preparation of Crystalline Tetrabromostearic Acid. The five liter flask containing the solution of fatty acids was clamped firmly into an ice-salt bath, the flask being at least three inches above the bottom of the bath to provide proper cooling. A mechanical stirrer with sufficient speed and power to produce good mixing was adjusted to about one half inch from the bottom of the flask. Bromine was added from a separatory funnel at such a rate that the temperature of the reaction mixture at no time exceeded 10°C . About 50 g of bromine were required for complete saturation, as indicated by the persistence of a bromine color. The crystalline crude tetrabromostearic acid which precipitated from the solution after standing overnight at -5°C was collected on a Buchner funnel, washed with redistilled petroleum ether and transferred to a dry five liter round bottom flask. Five liters of redistilled petroleum ether and 1.5 liters of ether, or more if necessary to effect complete solution, were added and the tetrabromostearic acid was brought into solution by refluxing on a steam bath. Twenty g of Norit were added, refluxing continued for a few minutes, and then the hot solution was filtered through a

warm Buchner funnel. Oversized filter paper was used in the funnel and was kept firmly in place by a water bath ring which fitted snugly in the funnel. The filtrate was allowed to stand overnight at -5°C . The product was filtered on a Buchner funnel and washed with redistilled petroleum ether. The white crystals were dried at room temperature and their melting point determined ($114-115^{\circ}$). If the melting point was low, the product was recrystallized from petroleum ether before proceeding.

Preparation of Methyl Linoleate. Two hundred g of tetrabromostearic acid and 200 g of granular zinc were mixed together and placed in a dry, ground-neck, round bottom flask. A condenser was attached and 200 ml of methyl alcohol were added and the acid dissolved by warming carefully on a steam bath. Cooling in a stream of tap water was necessary to control the initial reaction, after which the mixture was allowed to reflux for two hours on the steam bath. The reaction mixture was cooled and poured into a separatory funnel containing 500 ml of distilled water. A small amount of hydrochloric acid was added to decompose any zinc soaps which might be present and the mixture was shaken vigorously and allowed to stand until the esters had separated completely. The aqueous phase was then drawn off and extracted twice with 200 ml of redistilled petroleum ether. The extract was then washed with 500 ml of 2 percent sodium carbonate solution and twice with 100 ml of water. The washed ether solution was dried over anhydrous

sodium sulfate, filtered and the solvent removed by means of a water pump. The ester was distilled in an all glass vacuum still and the fraction collected that boiled at $135-140^{\circ}$, .1 mm pressure.

Preparation of 9, 12 Linoleic Acid. Two hundred g of the ester was placed in a five liter round bottom flask and saponified with 1200 ml of 5 percent alcoholic potassium hydroxide by standing overnight at room temperature. An equal volume of distill water was added and the mixture extracted twice with one half volumes of redistilled petroleum ether to remove any unsaponified ester. The saponified portion was then acidified with dilute hydrochloric acid (1:1) while cooling and shaking vigorously. The linoleic acid was extracted with an equal volume of 50 percent ethyl alcohol in water and dried with sodium sulfate. The solvent was removed under reduced pressure with a water pump and the acid distilled under a pressure of .1 mm. The portion which boiled at $150-155^{\circ}$ was collected and preserved by sealing in 15 ml glass tubes under high vacuum.

Preparation of Crystalline 10, 12 Linoleic Acid. Two hundred g of dehydrated castor oil was saponified in a solution of 10 g potassium hydroxide, 240 ml of ethyl alcohol and 20 ml water. After the saponification was complete, the solution was acidified with hydrochloric acid and the fatty acids extracted with redistilled petroleum ether, washed with water, dried over sodium sulfate and the solvent removed under reduced pressure. The fatty acids were then isomerized by dropping slow-

ly into a mixture of 400 g potassium hydroxide and 1 liter of ethylene glycol heated to 180°C, under vigorous stirring. The reaction mixture was covered with a nitrogen atmosphere during the whole process. The solution was heated for one-half hour with stirring after all the fatty acids had been added. The hot solution was poured over 1,000 g of chipped ice, acidified with hydrochloric acid and extracted with redistilled petroleum ether. The extract was washed with water and dried carefully over anhydrous sodium sulfate. The sulfate was then removed and the solution allowed to stand for 48 hours at -10°C. The crystalline acid was filtered off and recrystallized twice from redistilled petroleum ether and twice from ethanol. The yield of 10, 12 linoleic acid was 97 percent pure as calculated from the spectrophotometric readings.

Polymerization Process

The polymerization were conducted by bubbling air through the fatty acids at 60°C. for 150 hours. The air was dried by passing through a large calcium chloride tube and then freed from dust by filtering through cotton. The acids, 60 g each of conjugated and nonconjugated, were put into long Pyrex tubes of 18 mm diameter. These test tubes were suspended in a Pyrex jar containing mineral oil held at 60°C. The temperature was regulated to a constancy of $\pm 0.5^\circ\text{C}$ with the aid of an air stirrer designed in this laboratory and an Aminco thermostatically controlled heating unit. The air was introduced into the

acid by using drawn soft glass inlet tube connected to the purified air tube by rubber tubing. The flow of air was regulated by a series of screw clamps between the inlet tubes and the compressed air valve.

Three g samples of each acid were taken during intervals of 12, 24, 48, 100, and 150 hours. The samples taken were sealed in test tubes under high vacuum, and reserved for the determination of constants. The resulting viscous polymers were subjected to the depolymerization process.

Depolymerization Processes

Alkaline Depolymerization. Fifty g of the final viscous polymers from the autoxidation of linoleic acid was well mixed with 120 ml of 3 normal aqueous potassium hydroxide solution in a round bottom flask. The flask was clamped in an oil bath, attached to a condenser, and refluxed gently for 8 hours. The solution was then acidified with sulfuric acid (1:1) while hot, extracted with diethyl ether, dried with sodium sulfate, and allowed to stand overnight at -10°C . Any tar-like substance or precipitate which may have separated was removed by filtration. The solvent was removed under reduced pressure, and the residue saponified by refluxing with 4 times its weight of ethanol containing 2 percent by weight of sulfuric acid for 6 hours. Most of the alcohol was then removed under reduced pressure, and the residue dissolved in diethyl ether. The ether solution was washed first with water, then with dilute

sodium carbonate solution, and finally with water. The solution was dried with sodium sulfate and the solvent removed under reduced pressure. The residue was subjected to vacuum steam distillation. The monomers were volatile with steam and were obtained by extracting the distillate with petroleum ether. The extract was dried over sodium sulfate, and the solvent removed under reduced pressure. The residue was reserved for purification by molecular distillation. The polymers which were nonvolatile with steam were extracted with diethyl ether. After removal of the ether under reduced pressure, they were subjected to further depolymerization with acid.

Acid Depolymerization. The sample to be depolymerized was refluxed for 6 hours with 4 times its weight of anhydrous ethanol which contained 7 percent dry hydrochloric acid gas. The mixture was diluted with an equal volume of distilled water and extracted twice with redistilled petroleum ether. The ether extract was washed first with water then with dilute sodium bicarbonate solution and finally with water. It was dried over anhydrous sodium sulfate and the solvent removed under reduced pressure, the depolymerized product was ready for molecular distillation.

Molecular Distillation. The depolymerized product was dark brown in color, and was purified by molecular distillation. The molecular still used was of a short path film type and built in this laboratory (Plate I). In this type of still, the material to be distilled was allowed to flow by gravity along the inner

surface of a 28 mm tube. The outer surface of this tube was heated by means of a spiral of glass wire connected to a variac of one-half kilowatt capacity. The material was spread into a thin film by means of a glass spiral and the undistilled residue collected in a 50 ml round bottom flask. The distillate was collected on a water cooled jacket suspended in the center of the 28 mm tube. The distillate was allowed to flow by gravity into a 50 ml round bottom flask. The depolymerized product was passed through the still at 56°, 60° and 65°C.

Determination of Constants

Neutral Equivalent. A sample of the oxidized acid (0.1 g) was weighed out accurately and dissolved in 100 ml of ethanol. The mixture was shaken well and titrated with a standard 0.1 normal sodium hydroxide solution with phenolphthalein as indicator. A blank was run on the ethanol used as solvent. The neutral equivalent was calculated according to the following equation:

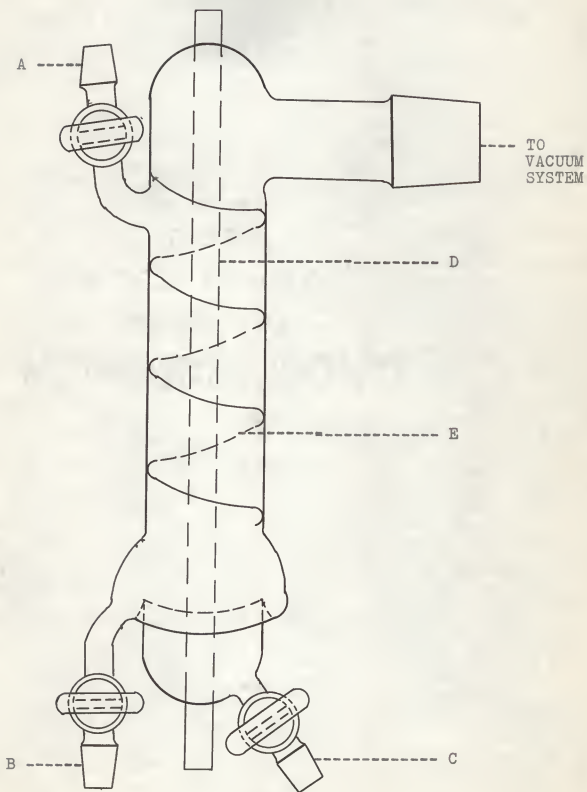
$$\text{Neutral equivalent} = \frac{\text{Wt. sample} \times 1,000}{\text{ml alkali} \times \text{normality}}$$

Molecular Weight. The cryoscopic method for molecular weight determination with benzene as solvent was used. Since the molecular weight to be determined was less than 1,000, which was comparatively small in the field of polymers and the solution used was quite dilute, the action of secondary valence forces (including especially hydrogen bonding) in effecting

EXPLANATION OF PLATE I

- A. Inlet
- B. Outlet for residue
- C. Outlet for distillate
- D. Condenser tube
- E. Glass spiral

PLATE I



molecular association was not serious. However, the molecular weights determined were for comparative use and were not considered to be accurate.

The apparatus used consists of a test tube with a side arm fitted with a cork which held a Beckman thermometer and a ring stirrer made from a small glass rod. The stirrer could be moved up and down through a piece of tubing inserted in the cork and the ring stirrer was not large enough to hit the thermometer bulb. The side arm was used for the purpose of admitting the solvent and solute. The tube was set into a larger test tube provided with a rubber ring, in order to minimize the cooling rate. The tube and jacket were inserted into an ice water mixture in a large beaker. Fifteen ml of benzene (thiophene free grade, recrystallized five times) was accurately measured and introduced into the tube. The stirrer was operated vigorously and the temperature at which the solid and liquid phases were in equilibrium was recorded as the freezing point of the solvent. The system was warmed and the freezing point again determined. Sufficient samples to give a depression of about 0.05°C . was accurately weighed, added to the solvent and the freezing point again determined. The molecular weight of the sample was then calculated from the equation:

$$\text{Molecular weight} = \frac{1,000 K_f g}{G \Delta T_f}$$

where ΔT_f was the observed depression of the freezing point caused by the addition of g grams of solute to G grams of solvent, K_f was the molar depression of the solvent which corresponds to the depression produced by a gram molecule of solute dissolved in 1,000 g of solvent.

Spectrophotometric Analysis of Conjugated Components. The ultraviolet absorption of the samples was determined by the use of a Beckman DU. Quartz Spectrophotometer. The sample of approximately 100 milligrams was weighed directly into a 100 ml volumetric flask. The sample was dissolved in carefully purified absolute ethyl alcohol and the flask filled to the mark. Aliquot portions of this solution were then diluted with the same solvent until the readings on the Beckman scale ($\log I/I_0$) was about 0.4-0.8. Readings at 2320, 2340, 2620, 2680, 2740, 3100, 3160, and 3220 Å were taken. The conjugated components in the sample were calculated from the equations:

$$K_2 = K_{2320} - 0.07$$

$$K_3 = 2.8 \left[K_{2680} - 1/2 (K_{2620} + K_{2740}) \right]$$

$$K_4 = 2.5 \left[K_{3160} - 1/2 (K_{3100} + K_{3220}) \right]$$

Where K_{2320} was the reading at 2320 Å, corrected to a concentration of 1 g solute in 1,000 ml solution, etc. The concentration of conjugated acids expressed as percentage of acid in sample was then calculated from the equations:

$$\text{Percentage conjugated diene acid} = \frac{100 K_2}{119}$$

$$\text{Percentage conjugated triene acid} = \frac{100 K_3}{214}$$

$$\text{Percentage conjugated tetraene acid} = \frac{100 K_4}{220}$$

Spectrophotometric Analysis of Nonconjugated Components.

About 0.1 g of sample was weighed out accurately into a small weighing vessel and placed in a marked ignition tube. Four ml of ethylene glycol (containing 7.5 percent of potassium hydroxide) was added. Nitrogen was blown in to displace air in the tube, stoppered and placed in wire basket. The basket was placed in an oil bath which had been heated to a temperature about 200° to 210°C. The oil bath was kept at 180°C for one-half hour, while the content of the tube was covered with nitrogen.

The contents were then transferred to 100 ml volumetric flasks, made up to volume using absolute ethyl alcohol, and allowed to stand in cold room overnight. The sample was brought to room temperature and filtered, the first 15-20 ml of filtrate were discarded. Aliquot portions of the filtrate were then diluted with absolute alcohol until the reading on the Beckman spectrophotometer was about 0.4-0.8. Two blanks were run along with the samples. Readings at 2320, 2340, 2620, 2680, 2740, 3100, and 3200 Å on the Beckman DU. Quartz Spectrophotometer were taken. The concentrations of nonconjugated

components in the sample expressed as percentage of acids were calculated from the equations:

$$K_2' = K'_{2320} + 0.4$$

$$K_3' = 4.1 \left[K'_{2680} - \frac{1}{2} (K'_{2620} + K'_{2740}) \right]$$

$$K_4' = 2.5 \left[K'_{3160} - \frac{1}{2} (K'_{3100} + K'_{3220}) \right]$$

and

$$K_2'' = K_2' - K_2$$

$$K_3'' = K_3' - K_3$$

$$K_4'' = K_4' - K_4$$

where K_2 to K_4 were values obtained in spectrophotometric analysis of conjugated components

then,

Percentage nonconjugated diene acid

$$= 1.125 K_2'' - 1.27 K_3'' + 0.04 K_4''$$

Percentage nonconjugated triene acid

$$= 1.87 K_3'' - 4.43 K_4''$$

Percentage nonconjugated tetraene acid

$$= 4.43 K_4''$$

RESULTS

Change in Molecular Weight and Neutral Equivalent During Autoxidation

The changes in molecular weight and neutral equivalent of the conjugated and nonconjugated linoleic acid when they are oxidized by bubbling air through them are shown by Figs. 1 and 2.

Effectiveness of the Depolymerization Processes

When the viscous polymers of nonconjugated linoleic acid was depolymerized by the alkaline process, only about 40 percent was depolymerized to monomer compounds. If the undecomposed fraction was subjected to the alkaline depolymerization process again, no appreciable change occurred. However, if this same undecomposed fraction was subjected to the acid depolymerization process, more than 50 percent of it was broken down to monomer products. When the original viscous polymers of nonconjugated linoleic acid was depolymerized by the acid process directly, more than 80 percent of it was broken down to monomers in one treatment.

The conjugated linoleic acid used before oxidation was a white crystalline solid. As oxidation proceeded, however, its melting point was decreased, and the final polymers obtained were a very viscous liquid at room temperature. When this

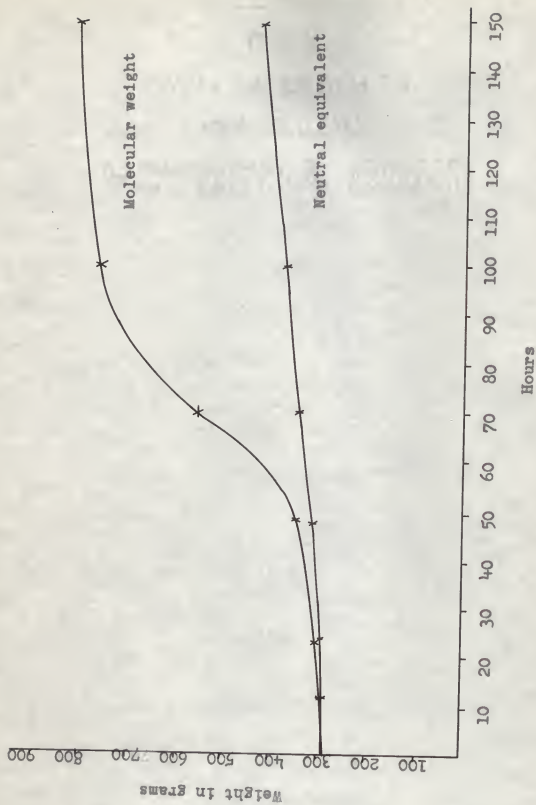


Fig. 1. Change in molecular weight and neutral equivalent of conjugated linoleic acid

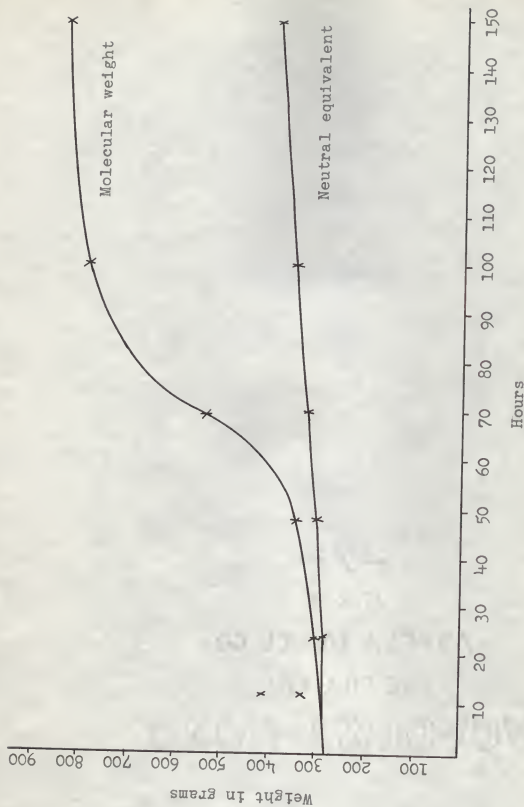


Fig. 2. Change in molecular weight and neutral equivalent of non-conjugated linoleic acid.

viscous liquid was depolymerized by the acid process, more than 80 percent was broken down to monomer products. The monomers thus obtained were a liquid at room temperature.

Products of Molecular Distillation

The depolymerized products were a dark brown colored liquid. After three runs in the molecular still at 56°, 60° and 65°C, more than 80 percent of them distilled as a pale yellow colored liquid. The molecular weights of these distillates ranged from 280 to 305. These distillates were then redistilled at 56°C, and the distillate redistilled again in a pot type molecular still. The distillate thus obtained was a colorless liquid, which when subjected to spectrophotometric analyses gave the compositions which are shown in Table 1.

Table 1. The composition of the depolymerization products of conjugated and nonconjugated linoleic acid polymers.

Composition (percent by weight)	Polymers of 9, 12 linoleic acid depoly- merized by alka- line process	Polymers of 9, 12 linoleic acid depoly- merized by acid process	Polymers of 10, 12 linoleic acid depoly- merized by acid process
conju. diene acid	2.3	1.9	35.6
nonconju. diene acid	61.5	42.2	0.0
conju. triene acid	1.3	0.4	11.8
nonconju. triene acid	2.3	2.7	8.3
conju. tetraene acid	0.0	0.0	0.0
nonconju. tetraene acid	0.0	0.0	0.0

DISCUSSION

The Formation of Trimers by Linoleic Acid

The data presented in this investigation showed that linoleic acid could be polymerized almost completely into trimers by autoxidation. This is somewhat contradictory to the papers published around 1940 (27, 28, 29). Bradley and Johnston (6) studied the polymerization of methyl linoleate at 300°C. under an atmosphere of carbon dioxide. They reported that most of the polymers formed were dimers, and only 6 percent were trimers. Overholt and Elm (20) also suggested that it was difficult to obtain trimers from linoleic acid. Their observation was based on the fact that linoleate forms a gel while linolenate of glycols dries to a hard film. However, four years later, Scanlan and Knight polymerized methyl oleate by bubbling air through it, and found a considerable portion of dimers. The present paper indicated that linoleic acid, either conjugated or nonconjugated, could be polymerized to trimers by air.

The Role of the Carboxyl Group in the Polymerization of Linoleic Acid

The molecular weights and neutral equivalents found in this investigation indicate that the increase in neutral equivalent during autoxidation of linoleic acid is less than 20 percent of the increase in molecular weight. If the linkage of the polymers is through double bonds, the neutral equivalent of the poly-

merized product should be kept constant, and if the binding between polymers is through carboxyl group, it should be increased at the same rate as the molecular weight. The present data indicated that more than 80 percent of the polymers formed during autoxidation of linoleic acid is due to the double bond. This is true for both conjugated and nonconjugated linoleic acid.

The close resemblance of the curves of the polymerized conjugated and nonconjugated linoleic acid obtained by plotting molecular weight and neutral equivalent separately against time should not be interpreted as indicating that identical mechanisms were involved in their polymerization. Furthermore, the work of this laboratory (1, 13) proved that the initial stages, especially the induction period, in the autoxidation of conjugated and nonconjugated linoleic acid are different. The depolymerization work in this paper also showed that the trimers of conjugated and nonconjugated linoleic acid gave different products upon depolymerization in the same way. Thus, the resemblance of these curves could indicate only that the periods prior to the occurrence of appreciable polymerization are the same for both conjugated and nonconjugated linoleic acid; after that period they also polymerized at about the same rate and to about the same molecular size.

The Differences in the Mechanisms Involved in the Polymerisation of Conjugated and Nonconjugated Linoleic Acid

During recent years, the suggestion that the Diels Alder diene reaction is the mechanism responsible for the polymerization of linoleic acid has become more and more promising. However, the results of the present investigation conflicted with this mechanism. A Diels Alder reaction could take place only when at least one of the reacting segments consists of a conjugated diene system. When a nonconjugated linoleic acid undergoes this type of polymerization, at least 50 percent of it has to be isomerized to conjugated acid in order to form dimers, or at least 75 percent should be isomerized in order to form trimers. This investigation showed that when a trimer of nonconjugated linoleic acid was depolymerized, less than three percent of conjugated diene acids could be found. A shifting of double bonds during depolymerization seemed to be impossible, because 9, 12 linoleic acid was obtained when the oxidation products of 9, 12 linoleic acid were depolymerized, as evidenced by the melting point of the bromo-addition derivative of the depolymerized product and its mixed melting point with tetrabromostearic acid prepared from the original 9, 12 linoleic acid.

The ease with which the viscous polymers were depolymerized by dry hydrochloric acid in ethanol could not be interpreted as an indication that the monomers were linked together by -C-O-C- linkages. Generally, an ether linkage between two secondary hydrocarbons is more easily cleaved than a carbon to carbon bond.

However, attachment of oxygen and the presence of unsaturation greatly influence the ease in which these linkages are broken. The hydrolytic cleavage of carbon to carbon bonds could take place readily when oxygen is attached to certain parts of the molecule. The residual unsaturation further promotes the ease of this type of cleavage.

The data presented in this paper added to the evidence that vinyl polymerization (XII) is the principal process responsible for the drying property of linoleic acid. The nature of the depolymerized products could be interpreted easily with this mechanism. The linolenic acid in the depolymerization products might have resulted from the formation of a third double bond in the linoleic acid segment by either dehydration of certain hydroxyl groups attached to the carbon chain or from the enolization of certain carbonyl group formed by the decomposition of peroxide.

SUMMARY

Linoleic acid, both conjugated and nonconjugated, were shown to be able to polymerize to viscous trimers by autoxidation at 60°C.

The carboxyl group in the linoleic acid was not the principal functional group for polymerization, more than 80 percent of the polymers formed during autoxidation were shown to be due to the double bonds.

The characteristics of the depolymerized products of conjugated and nonconjugated linoleic acid conflicted with the view that the Diels Alder reaction was the prominent one occurred in the polymerization of linoleic acid, and added to the evidence that vinyl polymerization was the principal process responsible for the drying property of linoleic acid.

ACKNOWLEDGMENT

The author wishes to express his appreciation to Dr. Fred A. Kummerow, major instructor, for assistance and supervision during this study.

LITERATURE CITED

- (1) Allen, R. R.
A study of the reaction of methyl linoleate with molecular oxygen. Unpublished M. S. thesis, Kansas State College, Manhattan, Kansas.
- (2) Bolland, J. L. and H. P. Koch.
The course of autoxidation reactions in polyisoprenes and allied compounds. Part 4, the primary thermal oxidation product of ethyl linoleate. Chem. Soc. Jour. 67: 445-448, 1945.
- (3) Bradley, T. F., E. L. Kropa and W. B. Johnston.
Drying oils and resins. Drying, non-drying and convertibility characteristics of maleic and succinic glycol polyesters. Indus. and Engin. Chem. 29: 1270-1276, 1937.
- (4) Bradley, T. F.
Drying oils and resins. Mechanism of the drying phenomena. Indus. and Engin. Chem. 29: 440-445, 1937.
- (5) Bradley, T. F.
Drying oils and resins. Polymeric functionality with relation to the addition polymerization of drying oils. Indus. and Engin. Chem. 30: 689-696, 1938.
- (6) Bradley, T. F. and W. B. Johnston.
Drying oils and resins. Reactions involving the carbon to carbon unsaturation during the thermal treatment of some esters of some unsaturated C_{18} fatty acids. Indus. and Engin. Chem. 32: 802-809, 1940.
- (7) Bradley, T. F. and others.
Drying oils and resins. Constitution of a drying oil gel. Indus. and Engin. Chem. 32: 694, 1940.
- (8) Bradley, T. F. and W. B. Johnston.
Drying oils and resins. Purification of polymerized methyl linoleate by molecular distillation. Indus. and Engin. Chem. 33: 86-89, 1941.
- (9) Burk, R. E. et al.
Polymerization and its application in the field of rubber, synthetic resins, and petroleum. New York: Reinhold, 312p. 1937.

- (10) Dean, H. K.
Utilization of fats. New York: Chemical Publishing Co., 1938.
- (11) Elm, A. C.
Antioxidants and the autoxidation of fats. Autoxidation of oleic acid, methyl oleate, oleyl alcohol, and cis-9-octadecene. Indus. and Engin. Chem. 31: 1425-1431, 1939.
- (12) Holman, R. T., W. O. Lundberg and G. O. Burr.
Spectrophotometric studies of the oxidation of fats. Part 2, the oxidation of diene fatty acids. Amer. Chem. Soc. Jour. 67: 1386-1934, 1945.
- (13) Jackson, A. H.
Differences in the autoxidation of linoleic and alkali conjugated linoleic acid. Unpublished M. S. thesis, Kansas State College, Manhattan, Kansas.
- (14) Kappelmeier.
Farben Ztg. 38: 1018, 1937.
- (15) Kropa, E. L. and T. F. Bradley.
Drying oils and resins. Insolubilization of maleic glycol polyesters by additive polymerization. Indus. and Engin. Chem. 31: 1512-1516, 1939.
- (16) Markley, K. S.
Fatty acids, their chemistry and physical properties. New York: Interscience Publishers, Inc., 668p. 1947.
- (18) Overholt, J. L. and A. C. Elm.
Formation and deterioration of paint films. Change in films of methyl esters of several unsaturated fatty acids under exposure to ultraviolet light. Indus. and Engin. Chem. 32: 378-383, 1940.
- (19) Overholt, J. L. and A. C. Elm.
Formation and deterioration of paint films. Change in films of glycol esters of several unsaturated fatty acids under exposure to ultraviolet light. Indus. and Engin. Chem. 32: 1348-1353, 1940.
- (20) Overholt, J. L. and A. C. Elm.
Formation and deterioration of paint films. Change in films of glyceryl esters of several unsaturated fatty acids under exposure to ultraviolet light. Indus. and Engin. Chem. 33: 658-660, 1941.

- (21) Powers, P. O., T. L. Overholt and A. C. Elm.
Formation and deterioration of paint films. *Indus. and Engin. Chem.* 35: 1257, 1941.
- (22) Powers, P. O.
Mechanism of the oxidation of drying oils. *Indus. and Engin. Chem.* 41: 304-309, 1949.
- (23) Rollett, A.
Linoleic acid. *Z. Physiol. Chem.* 62: 410, 1909.
- (24) Staudinger, H. et al.
Über Autoxydation organischer Verbindungen, 3. Über Autoxydation des asymm. Diphenyl-Aethylens. *Berichte* 58: 1075-1079, 1925.
- (25) Swern, D., J. T. Scanlan and H. B. Knight.
Catalytic air oxidation of methyl oleate and characterization of polymers formed. *Amer. Chem. Soc. Jour.* 67: 1132, 1945.
- (26) Swern, D., J. T. Scanlan and H. B. Knight.
Mechanisms of the reactions of oxygen with fatty materials. *Advances from 1941 through 1946. Amer. oil Chemists' Soc. Jour.* 25: 193, 1948.
- (27) Treibs, W.
Autoxidation of oxygen active acids. 5. Viscosimetric and volumetric analysis of the addition of oxygen to tri-glycerides. *Berichte.* 75B: 953-957, 1942.
- (28) Treibs, W.
Autoxidation of oxygen active acids. 8. Influence of dilution, monomeric 1, 2, and 1, 4, addition of oxygen to the conjugated double bond system of eleostearic acid and ricinenic acid esters. Autoxidative cleavage of the acid chains. *Berichte.* 76: 670-675, 1942.
- (29) Van Milusch, J. D.
Solid 10, 12, octadecadienoic acid- new linoleic acid melting at 57°C. *Amer. Chem. Soc. Jour.* 64: 1580, 1942.

Date Due

[illegible]